AD-A052 206 VERMONT UNIV BURLINGTON DEPT OF CHEMISTRY F/G 7/3
ORGANOSUBSTITUTED PHOSPHAZENES. X. REACTIONS OF HEXAFLUOROCYCLO--ETC(U)
MAR 78 J G DUPONT, C W ALLEN N00014-77-C-0605
UNCLASSIFIED TR-1 NL

| OF |
ADA
052206

END
DATE
FILMED
5-78
DDC

OFFICE OF NAVAL RESEARCH
Contract N0001477C-0605
Project NR 356-663
TECHNICAL REPORT No. 1

Organosubstituted Phosphazenes. X. Reactions of Hexafluorocyclotriphosphazene with Propenyl Lithium Reagents.

by

John G. DuPont and Christopher W. Allen*

Prepared for Publication

in

Inorganic Chemistry

University of Vermont
Department of Chemistry
Burlington, Vermont 05401

March 3, 1978

(14) TR-1

(12) 14 p.

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER: 1	2. GOVT ACCESSION NO.
3. RECIPIENT'S CATALOG NUMBER	
4. TITLE (and Subtitle): Organosubstituted Phosphazenes. X. Reactions of Hexafluorocyclotriphosphazene with Propenyl Lithium Reagents.	5. TYPE OF REPORT & PERIOD COVERED: Technical Report.
	6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s): John G. DuPont and Christopher W. Allen	8. CONTRACT OR GRANT NUMBER(s): N001477C-0605 (15) N00014-77-C-0685
9. PERFORMING ORGANIZATION NAME AND ADDRESS: Department of Chemistry, University of Vermont, Burlington, Vermont 05401	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS: Office of Naval Research, Department of the Navy, Arlington, Virginia 22217	12. REPORT DATE: March 3, 1978 (11) 3 Mar 78
	13. NUMBER OF PAGES: 13
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)	15. SECURITY CLASS. (of this report): Unclassified
	15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for Public Release, Distribution Unlimited

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

To be published in Inorganic Chemistry

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Hexafluorocyclotriphosphazene
Propenyl lithium Reagents
Fluorine-19 NMR
Mass spectrometry
Substitution Pathways

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The interactions of propenyl lithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) have been investigated. The reaction of either 1-propenyl or 2-propenyl lithium with $P_3N_3F_6$ proceeds with moderate to good yields to give the appropriate monosubstituted phosphazene. The potential for use of these materials as precursors to other organophosphazenes is shown by the occurrence of facile hydrogenation and bromination reactions. Although the addition of two equivalents of 2-propenyl lithium to $P_3N_3F_6$ results in degradation products, the addition of two equivalents of 1-propenyl lithium to $P_3N_3F_6$ results in the

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE

408 892

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

production of the geminally substituted phosphazene. Furthermore, the reaction of monophenylpentafluorocyclotriphosphazene with 1-propenyl lithium also yields a geminal derivative. These results are discussed in terms of the factors which control the substitution pattern observed in the reactions of organolithium reagents with $P_3N_3F_6$. The new propenyl fluorophosphazenes are characterized by infrared, nmr (proton and fluorine-19) and mass spectrometry.

Introduction

The reactions of cyclic and polymeric[2] fluorophosphazenes with organolithium reagents have proved to be a valuable method for producing a variety of organophosphazene derivatives. The reactions of alkyl-[3-6], alkynl-[7] and aryl lithium[2,8-10] reagents have been explored in detail, but, with the exception of a brief report of the synthesis of vinylpentafluorocyclotriphosphazene,[4] the reactions of alkenyl lithium reagents have not been reported. An investigation of the reactions of alkenyl lithium reagents with hexafluorocyclotriphosphazene ($P_3N_3F_6$) would be of interest in order to establish the factors which are significant in the control of the substitution pathway of the organolithium - fluorophosphazene reaction. Furthermore, the alkenylphosphazenes would be valuable precursors to a wide range of organophosphazenes derived from reactions at the olefinic center. These synthetic transformations would complement those which one could accomplish through reactions of phosphazenes with ketonic functions in the exocyclic group.[11] Therefore, we wish to report the synthesis and characterization of propenyl derivatives of $P_3N_3F_6$.

Experimental Section

Hexachlorocyclotriphosphazene (Ethyl Corp.) was converted to hexafluorocyclotriphosphazene[12] which in turn was converted to phenylpentafluorocyclotriphosphazene[8] by previously reported procedures. Diethyl ether was distilled from sodium/benzophenone. A mixture of cis and trans 1-bromopropene isomers (Aldrich) was distilled and stored over molecular sieves prior to use. The 2-bromopropene (Aldrich) was used without further purification. All reactions were carried out under anhydrous conditions and a nitrogen atmosphere. Lithium wire containing 1% sodium (PCR) was hammered into thin sheets and cut into small pieces. Concentrations of organolithium reagent solution were determined by quenching a 1 ml aliquot with water and titrating with 0.1m HCl to the methylred endpoint. NMR spectra in ($CDCl_3$) were obtained on a

JEOL C60-HL spectrophotometer at 60 MHz (^1H) or 56.5 MHz (^{19}F). Tetramethylsilane (^1H) and fluorotrichloromethane (^{19}F) were used as internal standards. Infrared spectra were obtained on thin films using a Beckman IR-20A spectrophotometer with sodium chloride or polyethylene disks. Mass spectra were obtained on a Perkin-Elmer RMU-6D spectrometer operating at 80 eV. Samples were introduced through the liquid inlet. Analytical samples were purified by preparative VPC using a Gow Mac 69-100 chromatography equipped with a DC 200 Chromsorb column. Elemental analyses were performed by Robertson Laboratories.

Preparation of 2-[1-propenyl]pentafluorocyclotriphosphazene (I).

In a typical experiment, 2.1 g. (0.3 moles) of lithium was placed in 100 ml. of diethyl ether followed by the slow addition of 17.0 g. (0.14 moles) of 1-bromopropene.[13] Following the metal-halogen exchanged reaction, the solution is allowed to sit for twelve hours at 0°C. in order to allow the LiBr to settle. After standardization, a sufficient amount of solution to provide 0.085 moles of the propenyl lithium was withdrawn by syringe and then added dropwise to a well-stirred solution of 19.0 g. (.076 moles) of $P_3N_3F_6$ in 50 ml. of diethyl ether. A cold water bath was used to cool the reaction. After addition of the lithium reagent, the solution was allowed to reflux for one hour. Pentane was then added to effect precipitation of the LiF and LiBr salts and the remaining solution was filtered. The solvent was removed under aspirator pressure and the resulting oil distilled (b.p. 41° -45°C. @ 1.5mm.) to give 10.5 g. (52% of theory) of product. Since the initial metal-halogen exchange reaction also produces small amounts of 1-propynyl-lithium,[13] there is a small amount of alkyne impurity in the product. The pure alkene may be obtained by preparative vapor phase chromatography. Anal. Calcd. for $P_3N_3F_5C_3H_5$: C, 13.29; H, 1.86; N, 15.51; mol. wt., 271. Found: C, 13.71; H, 1.71; N, 15.64; mol. wt., 271 (mass spectrum).

NMR: [14,15] ^{19}F $\delta(PF_2)63$(4F,J(PF) = 810Hz),δ(PFR)52(1F,J(PF) = 830 Hz.). IR: [16] 2980(m), 1630(m,CC str), 1280(s,PN str), 1070(w), 1000(s,Pf assym), 930(s,PF assym), 830(s,PF sym), 790(s,PF sym), 520(m), 470(m). Mass spectrum: 271(100%,$P_3N_3F_5C_3H_5^+$), 270(25%,$P_3N_3F_5C_3H_4^+$), 256(5%, $P_3N_3F_5C_2H_2^+$), 252(6%,$P_3N_3F_4C_3H_5^+$), 245(10%,$P_3N_3F_5CH_3^+$), 242(3%,$P_3N_3F_5C^+$), 231(75%,$P_3N_3F_5H^+$), 230(45%,$P_3N_3F_5^+$), 216(23%,$P_3N_2F_5^+$), 212(11%, $P_3N_3F_4H^+$), 211(10%,$P_3N_3F_4^+$), 197(18%,$P_3N_2F_4^+$), 171(13%,$P_2NF_5^+$), 167(7%,?) 152(8%, $P_2NF_4^+$), 133(4%,$P_2NF_3^+$), 114(14%,$P_2NF_2^+$), 107(6%,$PN_2F_2^+$), 69(30%, PF_2^+ and/or P_2N^+).

Preparation of 2,2-Di[1-propenyl]tetrafluorocyclotriphosphazene(II). In a typical experiment, 0.06 moles of 1-propenyl-lithium in 80 ml of diethyl ether was added dropwise, to a well stirred solution of 8.5 g (.03 moles) $P_3N_3F_6$ in 30 ml. of ether at 5°-10°C. After the addition was complete, the solution was allowed to reflux for three hours. Pentane was then added and the lithium salts filtered. The solvent was then removed under aspirator pressure to give an oil. The oil was distilled (b.p. 65°-70°C. @ 1.5 mm.) to give 5.0 g (48% of theory) of product. The compound was identified as geminal $P_3N_3F_4[CH = CHCH_3]_2$ on the basis of its mass spectrum (mol. wt.: Calcd.: 293, Found: 293 (mass spectrum) and its ^{19}F nmr spectrum. Attempts to prepare an analytical sample by VPC, resulted in compound decomposition. The material also decomposes slowly under ambiant conditions.

NMR: [14,15] ^{19}F $\delta(PF_2)64$(4F,J(PF) = 840Hz). IR: [16] 2950(m), 1630(m,CC str), 1280 (s,PN str), 1070(w), 1000(s,PF assym), 930(s,PF assym), 830(s), 790(s), 530(m), 490(m), 470(m). Mass spectrum: [17] 293(70%,$P_3N_3F_4C_6H_{10}^+$), 291(19%,$P_3N_3F_4C_6H_8^+$), 278(46%, $P_3N_3F_4C_5H_7^+$), 253(57%,$P_3N_3F_4C_3H_6^+$), 252(44%,$P_3N_3F_4C_3H_5^+$), 251(24%,$P_3N_3F_4C_3H_4^+$), 212 (33%,$P_3N_3F_4H^+$), 211(100%,$P_3N_3F_4^+$), 197(41%,$P_3N_2F_4^+$).

Preparation of 2-[1-propenyl]-2-phenyltetrafluorocyclotriphosphazene(III). In a typical experiment, .025 moles of 1-propenyl-lithium in 30 ml of diethyl ether was added, dropwise, to 6.0 g (.02 moles) $P_3N_3F_5C_6H_5$ in 30 ml. of ether. After the

initial exothermic reaction had subsided, the solution was allowed to reflux for 24 hours. The solution was then worked up as above to give 5.0 g of crude product. The crude product was shown by ^{19}F NMR to contain approximately 60% of the geminal compound the remainder being $P_3N_3F_5C_6H_5$. The mixture was redistilled carefully at 50° and 1 mmHg[7] to remove the $P_3N_3F_5C_6H_5$. The purified material (mol. wt. Calcd.: 329, Found 329 (mass spectrum[16])) retained a trace of starting material. The ^{19}F NMR spectrum did not show any of the non-geminal derivatives to be present.

NMR: [14,15] $\delta(PF_2)62(4F,J(PF) = 840Hz)$. IR: [16] 2980(w), 1635(m,CC str), 1600 (m,CC str), 1270(s,PN str), 940(s,PF assym), 840(s,PF sym), 580(m), 510(m), 490(m), 460(m). Mass spectrum:[18] 329(100%,$P_3N_3F_4C_9H_{10}^+$), 314(21%,$P_3N_3F_4C_8H_7^+$), 288(87%,$P_3N_3F_4C_6H_5^+$), 252(7%,$P_3N_3F_4C_3H_5^+$), 224(17%,$P_3N_3F_4CH^+$), 212(15%,$P_3N_3F_4H^+$), 211(1%,$P_3N_3F_4^+$), 197(69%,$P_3N_2F_4^+$), 167(12%,?), 152(24%,$P_2NF_4^+$), 149(18%,?); 141(8%,?), 133 (1%,$P_2NF_3^+$), 114(20%,$P_2NF_2^+$), 107(9%,PNF_2^+), 91(7%,$C_6H_5N^+$), 77(57%,$C_6H_5^+$).

Preparation of 2-[2-propenyl]pentafluorocyclotriphosphazene(IV). In a typical experiment, 100 ml. (.07 moles) of a previously prepared solution[19] of 2-propenyllithium in diethyl ether was added, dropwise, to a cooled, well stirred solution containing 18.0 g (.071 moles) $P_3N_3F_6$ in 50 ml of diethyl ether. The solution was allowed to reflux for one hour and worked up as before. The resulting oil was then distilled (b.p. 30°-32°C. @ 1.5mm) to give 6.0 g (32% of theory) of product. Anal. Calcd. for $P_3N_3F_5C_3H_5$: C, 13.30; H, 1.86; N, 15.51; mol. wt., 271. Found: C, 13.89; H, 1.76; N, 15.57; mol. wt., 271 (mass spectrum).

NMR [14] $\delta(PF_2)62(4F,J(PF) = 835Hz)$, $\delta(PFR)57(1F,J(PF) = 870Hz)$; ^1H: $\delta(PC\underline{H}trans)$ 6.2(1H,J(PH) = 2Hz), $\delta(PC\underline{H}cis)5.8(1H,J(PH) = 55Hz)$, $\delta(CH_3)2.0(3H,J(PH) = 18Hz)$. IR:[16] 2980(w), 1650(w,CC str), 1270(s,PN str), 1000(s,PF assym), 930(s,PF assym), 830(s,PF sym), 740(m,CH bend), 540(m), 500(m), 450(m). Mass spectrum: 271(69%,$P_3N_3F_5C_3H_5^+$), 256(4%,$P_3N_3F_5C_2H_2^+$), 252(4%,$P_3N_3F_4C_3H_5^+$), 245(3%,$P_3N_3F_5CH_3^+$), 231 (100%,$P_3N_3F_5H^+$),230 (18%,$P_3N_3F_5^+$), 216(7%,$P_3N_2F_5^+$), 212(12%,$P_3N_3F_4H^+$), 211(6%,$P_3N_3F_4^+$), 197(6%,$P_3N_2F_4^+$),

171(7%,$P_2NF_5^+$), 167(6%,?), 152(4%,$P_2NF_4^+$), 133(3%,$P_2NF_3^+$), 114(7%,$P_2NF_2^+$), 107 (3%,$PN_2F_2^+$), 69(14%, PF_2^+ and/or P_2N^+).

Reaction of $P_3N_3F_5C_3H_5$(I) with Phenyl lithium. A solution of I in diethyl ether was treated with an equimolar amount of phenyl lithium in diethyl ether. The reaction was allowed to proceed as above but only insoluble residues were obtained.

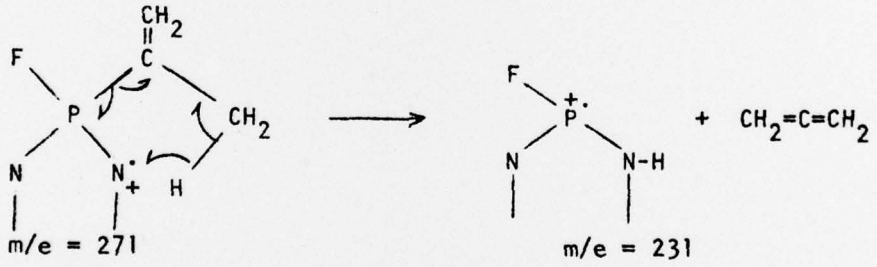
Attempted preparation of bis-[2-propenyl]pentafluorocyclotriphosphazene. The reaction of 2-propenyl lithium with $P_3N_3F_6$ on a 2:1 molar basis resulted only in the formation of insoluble residues.

Reactions of 2-propenylpentafluorocyclotriphosphazenes. Both I and II form the expected derivatives upon hydrogenation (H_2/Lindlar catalyst) or bromination (Br_2). The identity of the products was established by ^1H NMR spectroscopy.

Results and Discussion.

The reaction of one equivalent of 1-propenyl lithium with one equivalent of $P_3N_3F_6$ results in the production of the olefinic phosphazene, $P_3N_3F_5CH{=}CHCH_3$ (I). The fluorine-19 nmr data indicate the presence of the $P_3N_3F_5$ moiety and the expected phosphorus-nitrogen, phosphorus-fluorine and olefin[20] stretching frequencies are found in infrared spectrum. The molecular ion is the most intense ion in the mass spectrum. There are low intensity peaks which results from olefin fragmentation and loss of fluorine but the most significant fragments are m/e = 230 and 231 resulting from phosphorus-carbon bond cleavage. The latter peak may arise from hydrogen atom transfer to a ring nitrogen atom concomitant with the elimination of the organic fragment. The predominance of phosphorus-carbon over phosphorus-fluorine bond cleavage and the intensities of the $P_2NF_n^+$ linear ions is comparable to the behavior of the corresponding aryl derivatives.[10,21] Whereas doubly charged ions are significant in the aryl derivatives,[20] they are not observed in the mass spectra of the propenyl derivatives.

The reaction of one equivalent of 2-propenyl-lithium with $P_3N_3F_6$ proceeds, as expected, to give $P_3N_3F_5C(CH_3)=CH_2$ (IV). The yield of this compound is somewhat low, as compared to the previous reaction, and may be due to the fact that 2-propenyl-lithium is a more bulky nucleophile as compared to 1-propenyl-lithium or it may reflect the reactivity of the olefinic center in II. The identity of the product is confirmed by the nmr (fluorine-19 and proton), infrared and mass spectra. The mass spectra of I and IV are comparable in terms of the observed fragments but it is of interest to note that the most abundant species is now the $P_3N_3F_5H^+$ (m/e = 231) ion and the intensity of the $P_3N_3F_5^+$ is substantively reduced. A reasonable pathway for the formation of the $P_3N_3F_5H^+$ in the spectrum of IV involves a McLafferty rearrangement[22] of the molecular ion with the elimination of allene.



The reaction of two equivalents of 1-propenyl-lithium with one equivalent of $P_3N_3F_6$ results in the production of geminal $P_3N_3F_4(CH=CHCH_3)_2$ (II). In addition, the reaction of one equivalent of 1-propenyl-lithium with one equivalent of $P_3N_3F_5C_6H_5$ also gives the geminally substituted mixed organo tetrafluorocyclotriphosphazene, $P_3N_3F_4(C_6H_5)(CH=CH-CH_3)$ (III).

The infrared spectra of both II and III indicate the presence of olefinic (II and III) and aryl (III) groups. Note that there is no significant change in the C=C stretching frequency of II as compared to I.

The mass spectrum of II is interesting in that the high intensity ions result

from the successive cleavage of the propenyl substituents from the phosphazene ring. In fact, the 100% ion is the $P_3N_3F_4^+$ moiety which is different from the usual case where the molecular ion is the most intense. In the aryl analogs, this sort of behavior is typical of a geminal disposition of substituents.[21] The mass spectrum of III is also indicative of a geminally substituted material because of the high intensity of the ions resulting from loss of the organic substituents. The large relative abundance of the $P_3N_3F_4C_6H_5^+$ ion vs the $P_3N_3F_4C_3H_5^+$ ion is suggestive of a more facile cleavage of the propenyl-phosphorus than the phenyl-phosphorus bond. The question of the origin of this effect remains unclear. It could reflect either an inherent difference in carbon-phosphorus bond strengths or a differential in the ability of the two organic moieties to stabilize the resulting positive ion.

The geminal assignments for II and IIIare confirmed on the basis of the ^{19}F nmr spectra which allows one to assign geminal versus non-geminal structures unambiguously.[8] In geminal derivatives, only $\equiv PF_2$ resonances are observed, while in non-geminal derivatives both $\equiv PF_2$ and $\equiv PFR$ resonances are observed.

From this and previous data (Table I), it appears that geminal substitution is favored over non-geminal substitution in the reactions of organolithium reagents with $P_3N_3F_6$. Intuitively, one would expect a non-geminal pathway to be favored, at least on a steric basis. Furthermore, one would predict that a phosphorous atom bearing two fluorine atoms would be more positive than one bearing one organic substituent and one fluorine atom. The more positive atom would be more prone to nucleophilic attack, hence non-geminal substitution should result. This does not appear to be the case for organophosphazenes. The phosphorus atom bearing only one fluorine atom carries a larger partial positive charge due to the fact that the organic substituent can donate electron density to the phosphorus atom via and inductive mechanism. This causes the phosphorous d orbitals to expand in size. The

expanded d orbitals, however, can no longer have effective overlap with the small nitrogen lone pair orbitals, hence the phosphorous atom bears a partial positive charge while the nitrogen bears a partial negative charge. An example of this type of behavior is observed in the relative basicity of ring nitrogen atoms in $P_3N_3Cl_6$ and $P_3N_3(CH_3)_6$. While the equilibrium constant for protonation of the former is too low to be measured, the latter acts as a strong base towards a variety of Lewis acids.[24] Similarly, the $-N-P(C_6H)_2$ bond length in 2,2-$P_3N_3F_4(C_6H_5)_2$ is significantly longer than the remaining phosphorus-nitrogen bond in the ring.[25]

If geminal substitution is electrostatically favored, why does non-geminal substitution predominate when one equivalent of $P_3N_3F_6$ is reacted with two equivalents of phenyl-lithium (5% geminal, 95% non-geminal)[8] or two equivalents of o-tolyl-lithium (100% non-geminal)? It is believed that aryl-lithium reagents are in associated form in diethyl ether. One can thus rationalize non-geminal substitution as a result of a steric bulk of the attacking nucleophile. As evidence for this proposal, the reaction of one equivalent of $P_3N_3F_6$ with two equivalents of C_6H_5MgBr,[23] which is monomeric in THF, gives the geminal compound. Further support for this model is found in the reaction of one equivalent of $P_3N_3F_5C_6H_5$ with one equivalent of 1-propenyl-lithium, which results in the production of the geminal compound. If the aryl group were exerting a directive effect, one would expect non-geminal substitution, hence, the stereochemistry of the reaction would be independent of the incoming nucleophile. It therefore seems reasonable to conclude that geminal substitution is the most favored process and is controlled primarily by the incoming reagent. Non-geminal substitution will predominate only in cases where the incoming organo-metallic reagent is excessively bulky. Stereochemical control of phosphazene substitution reactions by the incoming nucleophile has previously been demonstrated for several reactions of amines with chlorocyclophosphazenes.[26]

Several attempts were made to synthesize $P_3N_3F_4(C(CH_3)=CH_2)_2$, however, only insoluble residues could be isolated. Apparently, addition of the second equivalent of 2-propenyl-lithium serves to initiate anionic attack on the olefinic center in IV. This type of behavior could also be the cause of the decreased yields of IV and of the insoluble residues observed in the reaction of I with phenyl lithium.

The reactions of I and IV with molecular hydrogen and bromine demonstrate the potential for the transformation of olefinic phosphazenes into a variety of new organophosphazenes.

Acknowledgement. This work was supported in part by the Office of Naval Research.

References and Notes

1. Part IX: C.W. Allen, R.L. Dieck, P. Brown, T. Moeller, C.D. Schmulbach and A. G. Cook, J.C.S. Dalton, 173 (1978).

2. H. R. Allcock, D. B. Patterson and T. L. Evans, J. Amer. Chem. Soc., 99, 6095 (1977).

3. T. Moeller, A. Failli and F. Y. Tsang, Inorg. Nucl. Chem. Lett., 1, 49 (1969).

4. E. Niecke, H. Thamm and O. Glemser, Z. Naturforsch., 26b, 366 (1971).

5. N. L. Paddock, T. N. Ranganathan and S. M. Todd, Can. J. Chem., 49, 164 (1971).

6. T. N. Ranathan, S. M. Todd and N. L. Paddock, Inorg. Chem., 12, 316 (1973).

7. T. Chivers, Inorg. Nucl. Chem. Lett., 7, 827 (1971).

8. C.W. Allen and T. Moeller, Inorg. Chem., 7, 2177 (1968).

9. T. Chivers and N. L. Paddock, Inorg. Chem., 11, 848 (1972).

10. C. W. Allen, P. L. Toch, M. Perlman, G. Brunst and J. C. Green, Chemical Institute of Canada/American Chemical Society Joint Conference, Abst. Inorg. 63, Montreal, (1977).

11. J. G. DuPont and C. W. Allen, Inorg. Chem., 16, 2964 (1977).

12. T. Moeller, K. John and F. Y. Tsang, Chem. Ind. (London), 347 (1961).

13. E. Braude and J. Cole, J. Chem. Soc., 2078 (1951).

14. Chemical shifts in ppm; coupling constants in Hz; all J(PF) values are based on a first-order approximation; R = alkenyl function.

15. ^{1}H nmr of the 1-propenyl derivatives are complex due to the fact that one is dealing with a mixture of cis and trans olefins. A reasonable simulation of the spectrum was obtained by using coupling constants from the literature and from the 2-propenyl phosphazene derivatives. However, due to the imprecise nature of this approach the data are not reported.

16. In cm^{-1}.

17. Several high mass/low intensity peaks are omitted.

18. Several low intensity peaks (<3%) are omitted. Peaks due to trace impurity of $P_3N_3F_5C_6H_5$ are omitted. When common fragments arise from III and $P_3N_3F_5C_6H_5$, the intensities of the fragments from III are corrected for the contributions from $P_3N_3F_5C_6H_5$.

19. Prepared from the reaction of lithium with 2-bromopropene.

20. L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Vo.. I, 3rd Ed., Wiley, New York, N.Y. (1975).

21. C. W. Allen and P. L. Toch, J.C.S. Dalton, 1685 (1974).

22. F. W. McLafferty in "Mass Spectrometry of Organic Ions," Ed. F. W. McLafferty, pg. 331, Academic Press, N.Y. (1963).

23. C. W. Allen, Chem. Comm., 152 (1970).

24. H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N.Y. (1972).

25. C. W. Allen, J. B. Faught, T. Moeller and I. C. Paul, Inorg. Chem., 8, 1719 (1969).

26. R. A. Shaw, Z. Naturforsch., 31b, 641 (1976); J.M.E. Goldschmidt and E. Licht, J.C.S. Dalton, 732 (1972); S.S. Krishnamurthy, A. C. Sau, A. R. Vasudeva Murthy, R. Keat, R. A. Shaw and M. Woods, J.C.S. Dalton, 1980 (1977).

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Office of Naval Research Arlington, Virginia 22217 Attn: Code 472	2
Office of Naval Research Arlington, Virginia 22217 Attn: Code 1021P	6
ONR Branch Office 536 S. Clark Street Chicago, Illinois 60605 Attn: Dr. Jerry Smith	1
ONR Branch Office 715 Broadway New York, New York 10003 Attn: Scientific Dept.	1
ONR Branch Office 1030 East Green Street Pasadena, California 91106 Attn: Dr. R. J. Marcus	1
ONR Branch Office 760 Market Street, R . 447 San Francisco, California 94102 Attn: Dr. P. A. Miller	1
Director, Naval Research Laboratory Washington, D. C. 20390 Attn: Code 6100	
The Asst. Secretary of the Navy (R&D) Department of the Navy Room 4E736, Pentagon Washington, D. C. 20350	1
Commander, Naval Air Systems Command Department of the Navy Washington, D.C. 20360 Attn: Code 310C (H. Rosenwasser)	1
Defense Documentation Center Building 5, Cameron Station Alexandria, Virginia 22314	12
U.S. Army Research Office P.O. Box 12211 Research Triangle Park, N.C.27709 Attn: CRD-AA-IP	1
Naval Ocean Systems Center San Diego, California 92152 Attn: Mr. Joe McCartney	1
Naval Weapons Center China Lake, California 93555 Attn: Head, Chemistry Division	1
Naval Civil Engineering Laboratory Port Hueneme, California 93041 Attn: Mr. W.S. Haynes	1
Professor O. Heinz Department of Physics & Chemistry Naval Postgraduate School Monterey, California 93940	1
Dr. A. L. Slafkosky Scientific Advisor Commandant of the Marine Corps (Code RD-1) Washington, D.C. 20380	1
Office of Naval Research Arlington, Virginia 22217 Attn: Dr. Richard S. Miller	1
ONR Branch Office Building 114, Section D 666 Summer Street Boston, Massachusetts 02210 Attn: Dr. L. H. Peebles	1

TECHNICAL REPORT DISTRIBUTION LIST

	No. Copies
Dr. T. C. Williams Union Carbide Corp. Chemicals and Plastics Tarrytown Technical Center Tarrytown, New York	1
Dr. R. Soulen Contract Research Dept. Pennwalt Corp. 900 First Avenue King of Prussia, Pennsylvania 19406	1
Dr. A. G. MacDiarmid University of Pennsylvania Department of Chemistry Philadelphia, Pennsylvania 19174	1
Dr. G. Dunks Union Carbide Corp. Corporate Research Laboratory Tarrytown Technical Center Tarrytown, New York 10591	1
Dr. A. Rheingold SUNY Plattsburgh Department of Chemistry Plattsburgh, New York 12901	1
Dr. C. Pittman University of Alabama Department of Chemistry University, Alabama 35486	1
Dr. H. Allcock Pennsylvania State University Department of Chemistry University Park, Pennsylvania 16802	1
Dr. M. Kenney Case-Western University Department of Chemistry Cleveland, Ohio 44106	1
Dr. R. Lenz University of Massachusetts Department of Chemistry Amherst, Massachusetts 01002	1
Dr. M. David Curtis University of Michigan Department of Chemistry Ann Arbor, Michigan 48105	1
Dr. M. Good University of New Orleans Department of Chemistry Lakefront New Orleans, Louisiana 70122	1
Douglas Aircraft Co. 3855 Lakewood Boulevard Long Beach, California 90846 Attn: Technical Library C1 290/36-84 AUTO-Sutton	1
NASA-Lewis Research Center 21000 Brookpark Road Cleveland, Ohio 44135 Attn: Dr. T. T. Serafini, MS 49-1	1
Dr. J. Griffith Naval Research Laboratory Chemistry Section, Code 6120 Washington, D.C. 20375	1
Dr. G. Goodman Globe-Union Inc. 5757 North Green Bay Avenue Milwaukee, Wisconsin 53201	1
Dr. E. Fischer, Code 2853 Naval Ship Research and Development Ctr. Annapolis Division Annapolis, Maryland 21402	1
Dr. Martin H. Kaufman, Head Materials Research Branch (Code 4542) Naval Weapons Center China Lake, California 93555	1
Dr. J. Magill University of Pittsburgh Metallurgical and Materials Engineering Pittsburgh, Pennsylvania 22230	1
Dr. D. Bergbreiter Texas A & M University Department of Chemistry College Station, Texas 77843	1